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(54) Title: BLEACHING COMPOSITIONS

(57) Abstract

The present invention relates to liquid hypohalite bleach-containing compositions which comprise a brightener and a radical scavenger, for effective fabric whiteness upon ageing of the compositions.

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Bleaching Compositions

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Field of the invention

10 The present invention relates to bleaching compositions, in particular to hypochlorite bleaching compositions, suitable for use in various laundry applications including hand and machine laundry methods.

15

Background of the invention

20 Bleaching compositions are well-known in the art. Amongst the different bleaching compositions available, those relying on bleaching by hypohalite bleaches such as hypochlorite are often preferred, mainly for performance reasons, especially at lower temperature.

25 However, a problem encountered with the use of hypohalite bleach-based compositions in laundry application is the resulting yellowing of the fabrics being bleached. This problem can be overcome by for example adding brighteners in hypohalite bleach-containing compositions.

30 However, when it is desired to incorporate brighteners in a liquid hypohalite bleach-based composition, the resulting composition generally shows a poor chemical stability upon ageing of the composition, resulting thereby in low whiteness performance of the composition when used in any laundry application after prolonged periods of storage. Indeed, upon prolonged storage periods the brighteners may be decomposed by the hypohalite bleach present in such a liquid hypohalite bleach-based composition, and 35 thus may lose its whitening potential. This brightener decomposition can be accelerated by product exposure at high temperature or by raw material impurities.

It is therefore an object of the invention to provide a hypohalite bleach-containing composition, suitable for use in laundry applications, which provides effective fabric whiteness performance to fabrics bleached therewith upon ageing of the composition before its use.

5 The Applicant has thus now surprisingly found that this problem is solved by formulating a liquid hypohalite bleaching composition comprising a brightener and a radical scavenger. Indeed, it has been found that the 10 addition of a radical scavenger in a liquid bleaching composition comprising a hypohalite bleach and a brightener, provides improved whiteness performance in any laundry application upon ageing of the composition, i.e. when used upon prolonged periods of storage after its manufacturing, as compared to the whiteness performance delivered by the same composition 15 without any radical scavenger, upon ageing of the composition. In other words, the use, in a liquid hypohalite bleach-containing composition comprising a brightener, of a radical scavenger, provides improved brightener stability in said composition.

20 In a preferred embodiment the compositions of the present invention further comprise a chelating agent and/or a pH buffering component.

Advantageously, the compositions of the invention are chemically stable. By "chemically stable", it is to be understood that the hypohalite bleaching 25 compositions of the present invention typically not undergo more than 25% loss of available chlorine after 5 days of storage at $50^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ and more preferably not more than 20%. The % loss of available chlorine may be measured using the method described, for instance, in "Analyses des Eaux et Extraits de Javel" by "La chambre syndicale nationale de L'eau de Javel et des produits connexes", pages 9-10 (1984). Said method consists in 30 measuring the available chlorine in the fresh compositions, i.e. just after they are made, and in the same compositions after 5 days at 50°C .

35 A further advantage of the compositions of the invention is that they are suitable for the bleaching of different types of fabrics including natural fabrics (e.g., fabrics made of cotton, viscose, linen, silk and wool), synthetic fabrics such as those made of polymeric fibers of synthetic origin as well as

those made of both natural and synthetic fibers. Indeed, the compositions of the present invention may be used on synthetic fibers despite a standing prejudice against the use of hypohalite bleaches, especially hypochlorite bleaches, on synthetic fibers, as evidenced by warning on labels of 5 commercially available hypochlorite bleaches and clothes. Advantageously the compositions of the present invention are not only safe to the fabrics per se bleached therewith but also to the fabrics colours.

Yet, another advantage of the liquid bleaching compositions of the present 10 invention is that said bleaching compositions are suitable for various laundry bleaching applications both when used in diluted conditions, e.g. as a detergent additive or a fully formulated laundry detergent composition, and when used in neat condition, e.g. as a liquid pretreater (spotter).

15

Background art

20 EP-A-668345 discloses hypochlorite-containing compositions comprising a source of strong alkalinity, a pH buffering means (silicate/carbonate) and radical scavengers. Optical brighteners are disclosed as optional ingredients without mentioning any, nor levels thereof.

25 EP-A-186 386, EP-A-206 718 and EP-A- 156 438 disclose hypochlorite-based compositions with brighteners, but fail to disclose the presence of radical scavengers.

30 EP-A-462 793 discloses hypochlorite-containing compositions with brighteners made hypochlorite resistant (the brighteners being transformed into a neutral ion-pair with a surface active quaternary ammonium ion-producing compound). No radical scavengers are mentioned.

35

Summary of the invention

The present invention is a liquid bleaching composition comprising

- a hypohalite bleach,
- from 0.001% to 1.0% by weight of the total composition of a brightener,
- 5 - and a radical scavenger.

In a preferred embodiment the compositions of the present invention further comprise a chelating agent and/or a pH buffering component. The presence of a chelating agent in the compositions of the present invention further 10 contributes to the brightener stability upon prolonged periods of storage, and thus to the effective whiteness performance of these compositions upon ageing. The presence of a pH buffering component in the compositions of the present invention further contributes to the effective whiteness performance of these compositions as well as to the fabric safety. Indeed, 15 the pH buffering component allows to control the alcalinity in the bleaching solution, i.e. maintain the pH of the bleaching solution at a pH of at least 7.5, preferably at least 8.5, and more preferably at least 9.5 for a longer period of time starting from the moment at which the dilution is completed (e.g. when the bleaching composition of the present invention is diluted in the bleaching 20 solution at a dilution level of 200:1 (water:composition)). This buffering action of the pH buffering component reduces the conversion of hypochlorite into hypochlorous acid, one of the species which are most responsible for fabric yellowing and/or fabric damage. The pH buffering component also contributes to the brightener stability in the wash solution and thus to the 25 effective whiteness performance of the compositions herein.

The present invention further encompasses the use, in a liquid hypohalite bleaching composition comprising a brightener, of a radical scavenger and/or chelating agent, for effective whiteness performance upon ageing of 30 the composition.

The present invention further encompasses the use, in a liquid hypohalite bleaching composition comprising a brightener, of a radical scavenger and/or chelating agent, for improved brightener stability in said composition 35 upon ageing of the composition.

Yet, the present invention also encompasses a method of bleaching fabrics where said fabrics are contacted with a bleaching composition according to the present invention, in its neat or diluted form.

5

Detailed description of the invention

10 Liquid bleaching compositions:

The compositions according to the present invention are in liquid form. Preferably, the compositions of the invention are in liquid aqueous form. More preferably, they comprise water in an amount of from 60% to 98% by weight, more preferably of from 80% to 97% and most preferably of from 15 85% to 97% by weight of the total aqueous liquid bleaching composition.

Hypohalite bleach

20 An essential component of the invention is a hypohalite bleach. Hypohalite bleaches may be provided by a variety of sources, including bleaches that are oxidative bleaches and subsequently lead to the formation of positive halide ions as well as bleaches that are organic based sources of halides such as chloroisocyanurates.

25

Suitable hypohalite bleaches for use herein include the alkali metal and alkaline earth metal hypochlorites, hypobromites, hypoiodites, chlorinated trisodium phosphate dodecahydrates, potassium and sodium dichloroisocyanurates, potassium and sodium trichlorocyanurates, N-30 chloroimides, N-chloroamides, N-chloroamines and chlorohydantoins.

35

For the liquid compositions herein, the preferred hypohalite bleaches among the above described are the alkali metal and/or alkaline earth metal hypochlorites selected from the group consisting of sodium, potassium, magnesium, lithium and calcium hypochlorites, and mixtures thereof, more preferably the alkali metal sodium hypochlorite.

Preferably, the liquid compositions according to the present invention comprise said hypohalite bleach such that the content of active halide in the composition is of from 0.1% to 20% by weight, more preferably from 0.25% to 8% by weight, most preferably from 0.5% to 6% by weight of the 5 composition.

The brightener

An essential component of the invention is a brightener or a mixture thereof. 10 Any brighteners known to those skilled in the art may be used herein including both hydrophobic and hydrophilic brighteners and mixtures thereof.

Brighteners are compounds which have the ability to fluoresce by absorbing ultraviolet wave-lengths of light and re-emitting visible light.

15 Brighteners, also referred to as fluorescent whitening agents (FWA), have been extensively described in the art, see for instance EP-A-0 265 041, EP-A-0 322 564, EP-A-0 317 979 or "Fluorescent whitening agents" by A.K. Sarkar, published by MERROW, especially page 71-72.

20 Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanine, dibenzothiophene-5,5-dioxide, azole, 5- and 6-membered-ring heterocycle, and other miscellaneous agents. Examples of such 25 brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982). Further optical brighteners which may also be used in the present invention include naphthlimide, benzoxazole, benzofuran, benzimidazole and any mixtures thereof. Particularly preferred brighteners 30 for use herein are the derivatives of stilbene and mixtures thereof.

Examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856. These brighteners include the PHORWHITE® series of brighteners from Verona.

35 Other brighteners disclosed in this reference include: Tinopal-UNPA®, Tinopal CBS® and Tinopal 5BM® available from Ciba-Geigy; Artic White CC® and Artic White CWD®; the 2-(4-styryl-phenyl)-2H-naphtho[1,2-

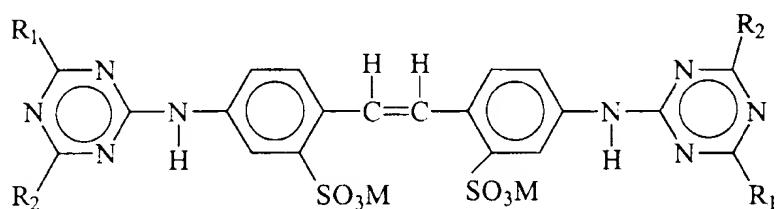
d]triazoles; 4,4'-bis(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins.

Specific examples of brighteners useful herein include 4-methyl-7-diethyl-
5 amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 1,3-diphenyl-
pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naptho-[1,2-
d]oxazole; 2-(stilbene-4-yl)-2H-naphtho[1,2-d]triazole, 3-phenyl-7-
(isoindolinyl) coumarin; 3-methyl-7-(isoindolinyl) coumarin; 3-chloro-7-
(isoindolinyl) coumarin; 4-(isoindolinyl)-4'-methylstilbene; 4-(isoindolinyl)-4'-
10 methoxystilbene; sodium 4-(isoindolinyl)-4'-stilbenesulfonate; 4-
(isoindolinyl)-4'-phenylstilbene; 4-(isoindolinyl)-3-methoxy-4'-methylstilbene;
4-(2-chloroisoindolinyl)-4'-(2-methylisoindolinyl)-2,2'-stilbenedisulfonic
acid; disodium 4,4'-diisoindolinyl-2,2'-stilbene disulfonate; 4,4'-diisoindolinyl-
2,2'-stilbenedisulfonamide; disodium 4,4'-(7,8-dichloro-1-isoindolinyl)2,2'-
15 stilbenedisulfonate; disodium 4,4'-(7-chloro-1-isoindolinyl)2,2'-
stilbenedisulfonate; disodium 4,4'-(6-isopropoxy-1-isoindolinyl)2,2'-
stilbenedisulfonate; disodium 4,4'-(7,8-diisopropyl-1-isoindolinyl)2,2'-
stilbenedisulfonate; disodium 4,4'-(7-butoxy-1-isoindolinyl)2,2'-
stilbenedisulfonate; disodium 4,4'-(6-trifluoromethyl-1-isoindolinyl)2,2'-
20 stilbenedisulfonate; disodium 4,4'-[6-(1,4,7-trioxanonyl)-1-isoindolinyl)]2,2'-
stilbenedisulfonate; disodium 4,4'-(7-methoxymethyl-1-isoindolinyl)2,2'-
stilbenedisulfonate; disodium 4,4'-(6-phenyl-1-isoindolinyl)2,2'-
stilbenedisulfonate; disodium 4,4'-(6-naphthyl-1-isoindolinyl)2,2'-
stilbenedisulfonate; disodium 4,4'-(6-methylsulfonyl-1-isoindolinyl)2,2'-
25 stilbenedisulfonate; disodium 4,4'-(7-cyano-1-isoindolinyl)2,2'-
stilbenedisulfonate; and disodium 4,4'-[7-(1,2,3-trihydroxypropyl)-1-
isoindolinyl)]2,2'-stilbenedisulfonate; disodium 4-isoindolinyl-4'-ethoxy-2,2'-
stilbenedisulfonate; disodium 4-isoindolinyl-4'-methoxy-2,2'-
stilbenedisulfonate; disodium 4-isoindolinyl-4'-ethoxy-2,2'-
30 stilbenedisulfonamide; disodium 4-isoindolinyl-4'-methyl-2,2'-
stilbenedisulfonamide; disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-
triazin-6-ylamino)stilbene-2:2 disulphonate, disodium 4,4'-bis-(2-morpholino-
4-anilino-s-triazin-6-ylamino)-stilbene-2:2'-disulphonate, disodium 4,4'-bis-
(2,4-dianilino -s-triazin-6-ylamino)-stilbene-2-sulphonate, monosodium 4,4"-
35 bis-(2,4-dianilino -s-triazin-6-ylamino)-stilbene-2:2'-disulphonate, disodium
4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-
ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-

2-yl)-stilbene-2,2' disulphonate, disodium 4,4'-bis-(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)-stilbene-2,2'-disulphonate, sodium 2-(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3-triazole-2''-sulphonate, 4,4'-bis-(2-sulphostyryl)-biphenyl, 4,4'-bis(4-phenyl-2H-1,2,3-triazol-2-yl)-2,2'-
5 stilbenedisulfonic acid and mixture thereof. See also U.S. Patent 3,646,015, U.S. Patent 3,346,502 and U.S. Patent 3,393,153 for further examples of brighteners useful herein.

Indeed one of the functionally equivalent derivative salts of 4,4'-bis(4-phenyl-2H-1,2,3-triazol-2-yl)-2,2'-stilbenedisulfonic acid, namely its sodium salt is available from Mobay Chemical Corporation, a subsidiary of Bayer AG under the name Phorwite® CAN. The amine salt is available from Molay under the name Phorwite® CL solution. The potassium salt is available under the name Phorwite® BHC 766.

15 Specific examples of hydrophilic optical brighteners useful in the present invention are those having the structural formula:



20 wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

25 When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-

5 stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-

10 2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Other substituted stilbene 2,2'-disulfonic acid derivatives also include 4-4'-

15 bis (2-2' styryl sulfonate) biphenyl, commercially available from Ciba-Geigy under the trade name Brightener 49® or other hydrophilic brighteners like for example Brightener 3® or Brightener 47®, also commercially available from Ciba-Geigy.

20 Specific examples of hydrophobic brighteners useful in the present invention include the polycyclic oxazole derivatives such as benzo-oxazole derivatives, or mixtures thereof and particularly preferred herein the benzo-oxazole derivatives. An example of such a brightener is benzoxazole,2,2'-(thiophenaldyl)bis having the following formula C18H10N2O2S, 25 commercially available from Ciba-Geigy under the trade name Tinopal SOP ®. This brightener is almost insoluble in water, i.e. it has a solubility being lower than 1 gram per liter. Another example of such a brightener is bis(sulfonylbenzofuranyl)biphenyl, commercially available from Ciba-Geigy under the trade name Tinopal PLC®.

30 By "hydrophobic brighteners", it is to be understood herein any brightener whose solubility in water is lower than 10 grams per liter at 25°C. By "solubility" of a given compound, it is to be understood herein the amount of said compound solubilized in deionized water at 25°C. Thus, a compound 35 having a solubility being lower than 10 grams per liter means that when less than 10 grams of said given compound is incorporated in deionized water at 25°C said compound is entirely dissolved in said water, i.e. a clear and

stable solution is obtained. In other words, incorporating 10 grams per liter or more of said given compound in water will result in a precipitation of said compound in said medium. Accordingly, by "hydrophilic brighteners", it is to be understood herein any brightener whose solubility in water is higher or 5 equal to 10 grams per liter at 25°C.

The compositions according to the present invention comprise from 0.001% to 1.0% by weight of the total composition of a brightener or a mixture thereof, preferably from 0.005% to 0.5%, more preferably from 0.005% to 10 0.3% and most preferably from 0.008% to 0.1%.

Where hydrophobic brighteners are present in the compositions herein they may both be solubilized or suspended in the hypohalite bleach-containing compositions of the present invention. Such brighteners solubilisation can 15 be for example achieved by means of a surfactant or a mixture thereof as described herein after. Various surfactants may be used for this purpose like C8-C20 alkyl aryl sulphonates as described for example in U.S. Patent 4, 623,476 or amine oxides as described for example in EP-A-186386. Preferred surfactants also called "co-surfactants" to solubilise and/or 20 suspend such a hydrophobic brightener are anionic surfactants including alkyl sulphates or alkylalkoxy sulphates having from 4 to 30 carbon atoms in the alkyl chain, or alkylethoxycarboxylates having from 6 to 30 carbon atoms in the alkyl chain such as Akyposoft® 100 NV from Chemy or Sandosan LNCS from Sandoz. Preferred are C12-C14 alkylalkoxysulphates. Such co- 25 surfactants herein should be used in amounts required to solubilize the hydrophobic brightener in need thereof.

Generally, when a co-surfactant is used, the liquid compositions of the present inventions are prepared in a process wherein the hydrophobic 30 brightener and the co-surfactant are first mixed to form a premix, before the premix is then mixed with the remainder of the composition which has been separately prepared.

Alternatively, the hydrophobic brightener may be suspended by means of a 35 specific suspending agent, like polymers and/or colloidal particulate silicate. Any polymers known to those skilled in the art as having suspending

properties are suitable for use herein including those described for example in EP-A- 206718.

The radical scavenger

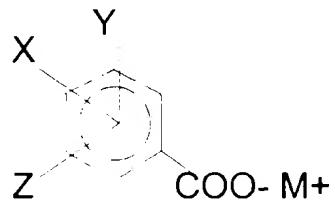
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An essential component of the invention is a radical scavenger or a mixture thereof. Naturally, for the purpose of the present invention, the radical scavengers have to be stable to the hypohalite bleach.

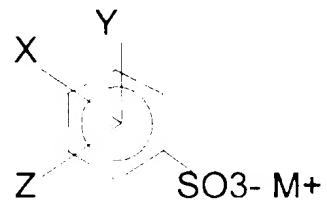
10 Suitable radical scavengers for use herein include aromatic radical scavengers comprising an unsaturated ring system of from 3 to 20 carbon atoms, preferably of from 3 to 18 and more preferably of from 5 to 14 and having a double bond set comprising a total of $4n+2$ electrons, wherein n is an integer of from 0 to 4, preferably of from 1 to 3. Indeed said aromatic
 15 radical scavengers include benzene derivatives, naphthalene derivatives, annulene derivatives, cyclopentadiene derivatives, cyclopropene derivatives and the like, especially aryl carboxylates and/or aryl sulfonates.

20 Particularly suitable radical scavengers (aryl carboxylates, aryl sulphonate and derivatives thereof) for use in the present invention have one of the following formulas:

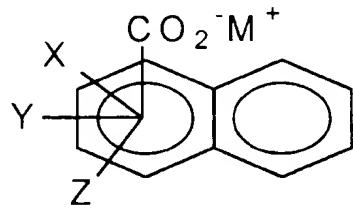
a)



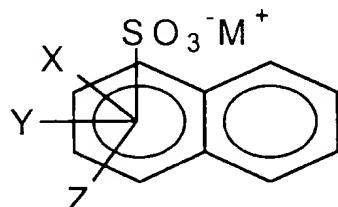
(b)



c)



d)



5

wherein each X, Y, and Z are -H, - COO-M^+ , -Cl, -Br, - $\text{SO}_3^- \text{M}^+$, - NO_2 , - OCH_3 , or a C₁ to C₁₀ primary and secondary alkyl groups and M is H or an alkali metal, or mixtures thereof. Examples of these components include pyromellitic acid, i.e. where X, Y and Z are - COO-H^+ ; hemimellitic acid, trimellitic acid, i.e. where X and Y are - COO-H^+ and Z is H. Preferred to be used in the present invention as radical scavengers are phthalic acid; sulfophthalic acid; other mono-substituted phthalic acids; di-substituted benzoic acids; alkyl-, chloro-, bromo-, sulfo-, nitro- and alkoxy- benzoic acids, i.e. where Y and Z are -H and X is a C₁ to C₁₀ primary and secondary alkyl groups, -Cl, -Br, - $\text{SO}_3^- \text{H}^+$, - NO_2 , and - OCH_3 respectively and substituted sulfonic acids. Preferred examples of the radical scavengers useful in the present invention are benzoic acid, methoxy benzoic acid, 3-nitrobenzoic acid, 4-toluene sulfonic acid, 2 n-octyl benzoic acid, 2 n-octyl sulfonic acid, anisic acid or salts thereof or mixtures thereof. Highly preferred examples of radical scavengers herein are benzoic acid and/or methoxy benzoic acid and/or 3-nitro benzoic acid.

All the radical scavengers described above are the acidic form of the species, i.e. M is H. It is intended that the present invention also covers the salt derivatives of these species, i.e. M is an alkali metal, preferably sodium or potassium. In fact, since the pH of the compositions of the present

invention is in the alkaline range, the radical scavengers of the present invention exist primarily as the ionized salt in the aqueous composition herein. The anhydrous derivatives of certain species described herein above can also be used in the present invention, e.g. pyromellitic 5 dianhydride, phthalic anhydride, sulphthalic anhydride and the like.

The compositions of the present invention comprise from 0.001% to 10% by weight of the total composition of a radical scavenger, or a mixture thereof, preferably from 0.01% to 8%, more preferably from 0.1% to 6% and most 10 preferably from 0.2% to 4%.

The present invention is based on the finding that the addition of a radical scavenger, in a liquid bleaching composition comprising a hypohalite bleach and a brightener, improves the chemical and physical stability of the 15 brighteners in said composition upon prolonged periods of storage time, thus resulting in effective whiteness performance of the aged composition when used in any laundry application.

By "effective" whiteness performance, it is to be understood that the 20 whitening performance delivered on fabrics bleached with an aged composition according to the present invention is improved, as compared to the whitening performance delivered by the same composition, but without any radical scavenger as mentioned herein before in the same aged condition. In other words, the present invention allows to maintain excellent 25 whitening performance after prolonged periods of storage time, as compared to the same composition, but without said radical scavenger.

The whitening effect, i.e. the yellowing-prevention effect of the present 30 invention upon ageing of the composition can be evaluated by comparing the composition according to the present invention to the same composition without the radical scavenger upon ageing of the compositions, typically after 3 months of storage at room temperature (around 25°C) after their manufacturing.

35 The degree of yellowing can be determined by both visual and instrumental grading. Visually, the difference in yellowing between items treated with different compositions can be determined by a team of expert panellists.

Instrumentally, the assessment can be determined with the help of Colorimeters such as Ganz Griesser® instruments (e.g., Datacolor® Spectraflash® SF 500, Machbet White-eye® 500) or a ZEISS ELREPHO® or others which are available for instance from Hunterlab® or Gardner®.

5

Optional chelating agents

In the compositions of the present invention, the presence of a chelating agent on top of the radical scavenger is not compulsory, but is highly 10 preferred. Naturally, for the purpose of the present invention, the chelating agents have to be stable to the hypohalite bleach.

Suitable chelating agents may be any of those known to those skilled in the 15 art such as the ones selected from the group comprising phosphonate chelating agents, phosphate chelating agents, polyfunctionally-substituted aromatic chelating agents, ethylenediamine N,N'- disuccinic acids, or mixtures thereof.

Chelating agents may be desired in the compositions of the present 20 invention, preferably phosphate chelating agents like phytic acid, as they further contribute to the benefit delivered by the radical scavengers herein by further improving the stability of the brighteners, thus delivering effective whiteness performance in any laundry application upon ageing of the compositions, i.e. after prolonged periods of storage. Thus, in its broadest 25 aspect the present invention encompasses the use, in a hypohalite bleaching composition comprising a brightener, of a chelating agent, for improved brightener stability in said composition as well as the use, in a hypohalite bleaching composition comprising a brightener, of a chelating agent, for effective whiteness performance upon ageing of the composition.

30

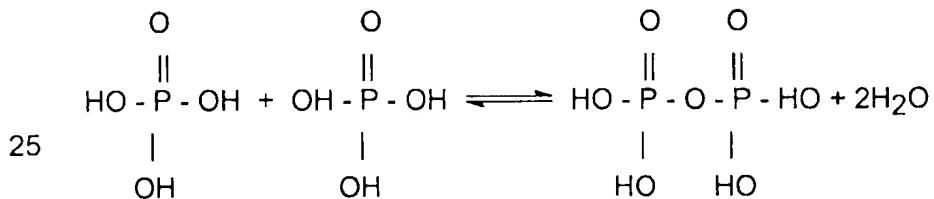
The presence of chelating agents may also contribute to reduce tensile strength loss of fabrics and/or colour damage, especially in a laundry pretreatment application. Indeed, the chelating agents inactivate the metal ions present on the surface of the fabrics and/or in the cleaning 35 compositions (neat or diluted) that otherwise would contribute to the radical decomposition of the hypohalite bleach.

Fabric safety may be evaluated by different test methods including the degree of polymerisation test method according to UNI (Ente Nazionale Italiano di Unificazione) official method UNI 8282-Determinazione della viscosità intrinseca in soluzione di cuprietilendiammina (CED).

5

Suitable phosphonate chelating agents for use herein may include alkali metal ethane 1-hydroxy diphosphonates (HEDP), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino aminotri(methylene phosphonic acid) (ATMP), nitrilo trimethylene phosphonates (NTP), ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates (DTPMP). The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonate (DTPMP) and ethane 1-hydroxy diphosphonate (HEDP). Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST®.

Suitable phosphate chelating agents are as following: Phosphonic acid can 20 be condensed in the reaction :



The reaction can be repeated with any of the reactive OH groups, and phosphate ingredients are obtained which can be

30 - linear or branched polyphosphates of structure

35 -when R is M or

- when M is a counterion, preferably alkali metal;
- when $0 \leq n+m < 500$ (if $n+m = 0$ then the compound is phosphonic acid)

5 - cyclic polyphosphates (also referred to as metaphosphates), of structure

-when R is M or

10

-if R is

15 the phosphate compound contains both cycles and branched chain, and can be referred to as an ultraphosphate.)

- where M is a counterion, preferably an alkali metal
- where $0 \leq n+m < 500$

20 All such phosphate ingredients are suitable for use herein, and preferred are linear phosphate ingredients (i.e. R is M) where n is 1 (pyrophosphate) and n is 2 (tripolyphosphate (STPP)), most preferably where n is 2. The most commonly available form of these phosphate is where M is Sodium.

25 Phytic acid, which is particularly suitable for use herein, is a hexaphosphoric acid that occurs naturally in the seeds of many cereal grains, generally in the form of the insoluble calcium-magnesium salt. It may also be derived from corn steep liquor. Commercial grade phytic acid is commercially available from J.T.Baker Co., e.g. as a 40% aqueous solution.

30 It is intended that the present invention covers the acidic form of phytic acid as well as alkali metal salt derivatives thereof, particularly sodium or potassium salts thereof. Sodium phytate is available from Jonas Chemical Co (Brooklyn, N.Y.). In fact since the typical pH of the compositions of the present invention are in the alkaline pH range, the phytic acid component 35 exists primarily as the ionized salt in the liquid compositions herein even if it is added in its acidic form. Mixtures of such salts of phytic acid are also covered.

Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are 5 dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'- disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine 10 N,N'- disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4, 704, 233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'- disuccinic acids is, for instance, commercially available under the tradename ssEDDS® from Palmer Research Laboratories.

15 Particularly preferred chelating agents for use herein are phosphate chelating agents like sodium pyrophosphate, sodium tripolyphosphate, phytic acid, and mixtures thereof.

20 Typically, the compositions according to the present invention comprise up to 10% by weight of the total composition of a chelating agent, or mixtures thereof, preferably from 0.01% to 5% by weight, more preferably from 0.05% to 2% and most preferably from 0.1% to 1.5%.

25 pH

The pH of the liquid compositions according to the present invention, as is, is typically from 12 to 14 measured at 25°C. The liquid compositions of the invention have a pH of from 7.5 to 13, preferably from 8 to 12, more 30 preferably from 8.5 to 11.5, when diluted into 1 to 500 times its weight of water. It is in this alkaline range that the optimum stability and performance of the hypohalite as well as fabric whiteness and/or safety are obtained. The pH range is suitably provided by the hypohalite bleach mentioned hereinbefore and optionally the pH buffering component when present, 35 which are alkalis. However, in addition to these components, a strong source of alkalinity may also optionally be used.

Suitable sources of alkalinity are the caustic alkalis such as sodium hydroxide, potassium hydroxide and/or lithium hydroxide, and/or the alkali metal oxides such as sodium and/or potassium oxide. A preferred strong source of alkalinity is a caustic alkali, more preferably sodium hydroxide 5 and/or potassium hydroxide. Typical levels of such caustic alkalis, when present, are of from 0.1% to 1.5% by weight, preferably from 0.5% to 1.5% by weight of the composition.

10

Optional pH buffering components

In the compositions of the present invention, the presence of a pH buffering 15 component is not compulsory, but is highly preferred.

The pH buffering component ensures that the pH of the composition is buffered to a pH value ranging from 7.5 to 13, preferably from 8 to 12, more preferably from 8.5 to 11.5 after the composition has been diluted into 1 to 20 500 times its weight of water.

Suitable pH buffering components for use herein are selected from the group consisting of alkali metal salts of carbonates, polycarbonates, sesquicarbonates, silicates, polysilicates, boron salts, phosphates, 25 stannates, alluminates and mixtures thereof. The preferred alkali metal salts for use herein are sodium and potassium.

Suitable boron salts or mixtures thereof for use herein include alkali metal salts of borates and alkyl borates and mixtures thereof. Examples of boron 30 salts include boric acid, alkali metal salts of metaborate, tetraborate, octaborate, pentaborate, dodecaboron, boron trifluoride and alkyl borate containing from 1 to 12 carbon atoms, preferably from 1 to 4. Suitable alkyl borate includes methyl borate, ethyl borate and propyl borate. Particularly preferred boron salts herein are the alkali metal salts of metaborate, such as 35 sodium metaborate, potassium metaborate, and the alkali metal salts of borate, such as sodium borate, or mixtures thereof. Boron salts like sodium metaborate and sodium tetraborate are commercially available from Borax

and Societa Chimica Larderello under the name sodium metaborate and Borax®.

Particularly preferred pH buffering components are selected from the group 5 consisting of sodium carbonate, sodium silicate, sodium borate, sodium metaborate and mixtures thereof.

The raw materials involved in the preparation of hypohalite bleaches usually 10 contain by-products, e.g. calcium carbonate resulting in an amount of up to 0.4% by weight of by-product within the hypohalite composition. However, at such amount, the by-product will not have the buffering action defined above.

Liquid bleaching compositions herein will contain an amount of pH buffering 15 component of from 0.5% to 9% by weight, preferably from 0.5% to 5% by weight, and more preferably in an amount of from 0.6% to 3% by weight of the composition.

The composition according to the invention may comprise other optional 20 components such as bleach-stable surfactants, organic or inorganic alkalis, builders, thickening agents, polymers, pigments, dyes, solvents, perfumes, and mixtures thereof.

Optional surfactants

25 The liquid compositions of the present invention may further comprise a surfactant or a mixture thereof as a desirable optional ingredient. Said surfactants may be present in the compositions according to the present invention in amounts of from 0.1% to 50% by weight of the total composition, 30 preferably of from 0.1% to 40% and more preferably of from 1% to 30%.

Surfactants suitable for use herein include anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof.

35 Suitable anionic surfactants for use in the compositions herein include water-soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a

C₁₀-C₂₄ hydrocarbyl, preferably linear or branched alkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ linear or branched alkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, 5 and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

10 Other suitable anionic surfactants for use herein are water-soluble salts or acids of the formula RO(A)_mSO₃M wherein R is an unsubstituted C₆-C₂₄ linear or branched alkyl group having a C₆-C₂₄ alkyl component, preferably a C₁₀-C₂₀ linear or branched alkyl, more preferably C₁₂-C₁₈ linear or branched alkyl, A is an ethoxy or propoxy unit, m is greater than zero, 15 typically between about 0.5 and about 30, more preferably between about 0.5 and about 5, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific 20 examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperidinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate, C₁₂-C₁₈E(1.0) sulfate, C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulfate, C₁₂-C₁₈E(2.25) sulfate, C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulfate, C₁₂-C₁₈E(3.0) sulfate, and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate, C₁₂-C₁₈E(4.0) sulfate, wherein the counterion 25 is conveniently selected from sodium and potassium.

30 In a particularly preferred embodiment of the present invention the surfactant system used is an anionic surfactant system, namely alkyl alkoxy (preferably ethoxy) sulphate alone like alkyl (ethoxy) 3 sulphate or together with a co-surfactant, preferably a C₂-C₁₀ alkyl sulphate and/or a C₈-C₂₂ alkyl or aryl 35 sulphonate like C₈-C₂₂ benzene sulphonate and/or another alkyl alkoxy sulphate apart the 3 ethoxylated one. Indeed the presence of said alkyl (ethoxy) 3 sulphate alone or together with a cosurfactant provides the

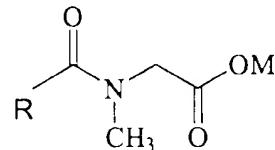
desired viscosity to the present compositions and delivers excellent stain removal properties to said compositions especially when used in any laundry application.

5 Typically such compositions according to the present invention have a viscosity between 25 cps and 1500 cps, preferably between 50 cps and 1100 cps, depending from the ratio between AE₃S and the co-surfactant, when measured with a rheometer like carri-med CSL2-100® at the following viscosity parameters : angle : 1°58, gap : 60, diameter : 4.0 cm, iner : 63.60
10 at a temperature of 25°C and a shear rate of 30 1/sec.

Other anionic surfactants useful for detergents purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and
15 triethanolamine salts) of soap, C₉-C₂₀ linear alkylbenzenesulfonates, C₈-C₂₂ primary or secondary alkanesulfonates, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycolethersulfates (containing
20 up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C₁₄-C₁₆ methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate
25 (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the
30 formula RO(CH₂CH₂O)_kCH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and
35 Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued

December 30, 1975, to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Other suitable anionic surfactants for use herein also include acyl
5 sарcosinate or mixtures thereof, in its acid and/or salt form, preferably long
chain acyl sarcosinates having the following formula:



10 wherein M is hydrogen or a cationic moiety and wherein R is an alkyl group of
from 11 to 15 carbon atoms, preferably of from 11 to 13 carbon atoms.
Preferred M are hydrogen and alkali metal salts, especially sodium and
potassium. Said acyl sarcosinate surfactants are derived from natural fatty
15 acids and the amino-acid sarcosine (N-methyl glycine). They are suitable to
be used as aqueous solution of their salt or in their acidic form as powder.
Being derivatives of natural fatty acids, said acyl sarcosinates are rapidly and
completely biodegradable and have good skin compatibility.

Accordingly, suitable long chain acyl sarcosinates to be used herein include
20 C₁₂ acyl sarcosinate (i.e., an acyl sarcosinate according to the above formula
wherein M is hydrogen and R is an alkyl group of 11 carbon atoms) and C₁₄
acyl sarcosinate (i.e., an acyl sarcosinate according to the above formula
wherein M is hydrogen and R is an alkyl group of 13 carbon atoms). C₁₂ acyl
25 sarcosinate is commercially available, for example, as Hamposyl L-30[®]
supplied by Hampshire. C₁₄ acyl sarcosinate is commercially available, for
example, as Hamposyl M-30[®] supplied by Hampshire.

Suitable nonionic surfactants for use herein include a class of compounds
30 which may be broadly defined as compounds produced by the condensation
of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic
compound, which may be branched or linear aliphatic (e.g. Guerbet or
secondary alcohol) or alkyl aromatic in nature. The length of the hydrophilic
or polyoxyalkylene radical which is condensed with any particular
35 hydrophobic group can be readily adjusted to yield a water-soluble
compound having the desired degree of balance between hydrophilic and

hydrophobic elements. Accordingly suitable nonionic synthetic surfactants include :

5 (i) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 20 carbon atoms in either a straight chain or branched chain configuration, preferably from 8 to 12 carbon atoms, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol.

10 10 The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, and nonane;

15 (ii) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. Examples are compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11000 resulting from the reaction of 20 ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000;

25 (iii) The condensation product of aliphatic alcohols having from 6 to 22 carbon atoms, in either straight chain or branched chain configuration, preferably from 8 to 18 carbon atoms, with from 2 to 35 moles of ethylene oxide, preferably from 4 to 25 and more preferably from 5 to 30 18. Examples of this type of material are a coconut alcohol ethylene oxide condensate having from 5 to 18 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 9 to 14 carbon atoms;

35 (iv) Trialkyl amine oxides and trialkyl phosphine oxides wherein one alkyl group ranges from 10 to 18 carbon atoms and two alkyl groups range from 1 to 3 carbon atoms; specific example is tetradecyl dimethyl phosphine oxide;

(v) The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol; The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide.

Particularly suitable nonionic surfactants for use herein are capped nonionic ethoxylated surfactants according to the formula:



wherein R_1 is a C₈-C₁₈ linear or branched alkyl or alkenyl group, aryl group, alkaryl group, preferably, R_1 is a C₁₀-C₁₅ alkyl or alkenyl group, more preferably a C₁₀-C₁₅ alkyl group;

20 R_2 is a C₂-C₁₀ linear or branched alkyl group, preferably a C₄ group; R_3 is a C₁-C₁₀ alkyl or alkenyl group, preferably a C₁-C₅ alkyl group, and n is an integer ranging in the range of from 1 to 20, preferably from 1 to 10, more preferably from 1 to 5; or mixtures thereof.

25 These surfactants are commercially available from BASF under the trade name Plurafac®, from HOECHST under the trade name Genapol® or from ICI under the trade name Symperonic®. Preferred capped nonionic ethoxylated surfactant of the above formula are those commercially available under the tradename Genapol® L 2.5 NR from Hoechst, and Symperonic® LF/CS 1100 from ICI.

Other suitable nonionic surfactants for use herein include the amine oxides corresponding to the formula:



wherein R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R" are, each, independently, an alkyl group containing 1 to 6 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. The preferred amine oxides are those

5 in which the primary alkyl group has a straight chain in at least most of the molecules, generally at least 70%, preferably at least 90% of the molecules, and the amine oxides which are especially preferred are those in which R contains 10-18 carbons and R' and R" are both methyl. Exemplary of the preferred amine oxides are the N-hexyldimethylamine oxide, N-

10 octyldimethylamine oxide, N-decyldimethylamine oxide, N-dodecyl dimethylamine oxide, N-tetradecyldimethylamine oxide, N-hexadecyl dimethylamine oxide, N-octadecyldimethylamine oxide, N-

15 eicosyldimethylamine oxide, N-docosyldimethylamine oxide, N-tetracosyl dimethylamine oxide, the corresponding amine oxides in which one or both of the methyl groups are replaced with ethyl or 2-hydroxyethyl groups and mixtures thereof. A most preferred amine oxide for use herein is N-decyldimethylamine oxide.

Other suitable nonionic surfactants for the purpose of the invention are the

20 phosphine or sulfoxide surfactants of formula :

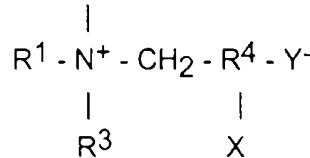


wherein A is phosphorus or sulfur atom, R is a primary alkyl group

25 containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R" are, each, independently selected from methyl, ethyl and 2-hydroxyethyl. The arrow in the formula is a conventional representation of a semi-polar bond.

30 Suitable zwitterionic detergents for use herein comprise the betaine and betaine-like detergents wherein the molecule contains both basic and acidic groups which form an inner salt giving the molecule both cationic and anionic hydrophilic groups over a broad range of pH values. Some common examples of these detergents are described in U.S. Pat. Nos. 2,082,275,

35 2,702,279 and 2,255,082, incorporated herein by reference. Preferred zwitterionic detergent compounds have the formula :
R²



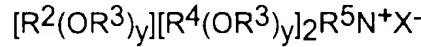
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wherein R1 is an alkyl radical containing from 8 to 22 carbon atoms, R2 and R3 contain from 1 to 3 carbon atoms, R4 is an alkylene chain containing from 1 to 3 carbon atoms, X is selected from the group consisting of hydrogen and a hydroxyl radical, Y is selected from the group consisting of carboxyl and sulfonyl radicals and wherein the sum of R1, R2 and R3 radicals is from 14 to 24 carbon atoms.

Amphoteric and ampholytic detergents which can be either cationic or anionic depending upon the pH of the system are represented by detergents such as dodecylbeta-alanine, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072, N-higher alkylaspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the trade name "Miranol", and described in U.S. Pat. No. 2,528,378, said patents being incorporated herein by reference. Additional synthetic detergents and listings of their commercial sources can be found in McCutcheon's Detergents and Emulsifiers, North American Ed. 1980, incorporated herein by reference.

Cationic surfactants suitable for use in compositions of the present invention are those having a long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula:

30

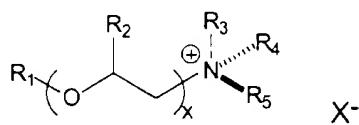


wherein R² is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, benzyl ring structures formed by joining the two R⁴ groups, and hydrogen when y is not 0; R⁵ is

the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

5

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



10

Formula I

whereby R₁ is a short chainlength alkyl (C₆-C₁₀)

y is 2-4, preferably 3.

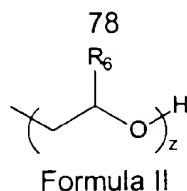
whereby R₂ is H or a C₁-C₃ alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

15 whereby R₃, R₄ and R₅ are either the same or different and can be either a short chain alkyl (C₁-C₃) or alkoxylated alkyl of the formula II,

whereby X⁻ is a counterion, preferably a halide, e.g. chloride or methylsulfate.

20



Formula II

R₆ is C₁-C₄ and z is 1 or 2.

25

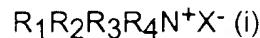
Preferred quat ammonium surfactants are those as defined in formula I whereby

R₁ is C₈, C₁₀ or mixtures thereof, x=0,

R₃, R₄, R₅ = CH₃.

30

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein R₁ is C₈-C₁₆ alkyl, each of R₂, R₃ and R₄ is independently C₁-C₄ alkyl, benzyl, and -(C₂H₄₀)_xH where x has a value from 2 to 5, and X is an anion. Not more than one of R₂, R₃ or R₄ should be benzyl.

The preferred alkyl chain length for R₁ is C₁₂-C₁₅ particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R₂R₃ and R₄ are methyl and the anion X may be selected from halide, methosulphate, acetate and phosphate ions. Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;
decyl triethyl ammonium chloride;
C₁₂-15 trimethyl ammonium chloride or bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;
choline esters (compounds of formula (i) wherein R₁ is
CH₂-CH₂-O-C-C₁₂-14 alkyl and R₂R₃R₄ are methyl).



di-alkyl imidazolines

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

Optional polymers

An optional component of the compositions herein is a polymer. That polymer, has surprisingly been found to also reduce the yellowing of the fabrics treated therewith, i.e. improve whiteness, as well as improve fabric safety. Naturally, for the purpose of the invention, the polymer has to be stable to the hypohalite bleach.

Suitable polymers for use are polymers comprising monomeric units selected from the group consisting of unsaturated carboxylic acids, polycarboxylic acids, sulphonic acids, phosphonic acids and mixtures thereof. Co-polymerisation of the above monomeric units among them or with other co-monomers such as styrenesulfonic acid is also suitable.

Preferred examples of such polymers are the polymers and co-polymers of monomeric units selected from the group consisting of acrylic acid, maleic acid, vinylsulphonic acid and mixtures thereof. Also suitable for use herein are the above mentioned polymers and co-polymers which are modified in order to contain other functional groups such as aminophosphonic and/or phosphonic units. More preferred polymers are selected from the group consisting of polyacrylate polymers, co-polymers of acrylic and maleic acid, co-polymers of styrene sulphonic acid and maleic acid, and mixtures thereof, preferably modified with aminophosphonic and/or phosphonic groups.

The molecular weight for these polymers and co-polymers is preferably below 100,000, most preferably between 500 and 50,000. Most suitable polymers and co-polymers for use herein will be soluble in an amount up to 0.1% by weight, in an aqueous composition comprising 5% by weight of sodium hypochlorite with its pH adjusted to 13 with sodium hydroxide.

Commercially available such polymers, suitable for use herein, are the polyacrylate polymers sold under the tradename Good-Rite® from BF Goodrich, Acrysol® from Rohm & Haas, Sokalan® from BASF, Norasol® from Norso Haas. Also suitable for use herein are the co-polymers of styrene sulphonic acid and maleic acid, commercially available under the tradename Versaflex® from National Starch such as Versaflex 157, as well as Acumer® terpolymers from Rohm and Haas, in particular Acumer® 3100. Preferred commercially available polymers are the polyacrylate polymers, especially the Norasol® polyacrylate polymers and more preferred are the polyacrylate polymer Norasol® 410N (MW 10,000) and the polyacrylate polymer modified with phosphonic groups Norasol® 440N (MW 4000) and its corresponding acid form Norasol® QR 784 (MW 4000).

A preferred polymer for use herein is a polyacrylate polymer modified with phosphonic groups commercially available under the tradename Norasol® 440N (MW 4000) and its corresponding acid form Norasol® QR 784 (MW 4000) from Norso-Haas.

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Mixtures of polymers as herein described may also be used in the present invention.

10 Polymers herein are preferably present in low amounts, i.e. in amounts of up to 10%, preferably up to 1%, more preferably up to 0.5% by weight, even more preferably from 0.001% to 0.3% by weight, and most preferably from 0.005% to 0.2% by weight of the liquid composition.

15 Method of bleaching fabrics:

Particularly preferred surfaces to be bleached with the compositions herein are fabrics including for example clothes, curtains, drapes, bed linens, bath linens, table cloths, sleeping bags, tents, upholstered furniture and the like, 20 and carpets.

Thus, the present invention further encompasses a method of bleaching fabrics which comprises the step of contacting said fabrics with a bleaching composition according to the present invention. In a preferred embodiment, 25 the compositions used in said method of bleaching fabrics are liquid hypochlorite-containing compositions that may further comprise a chelating agent and/or a pH buffering component as defined hereinbefore. Said method according to the present invention delivers effective whiteness performance upon ageing of the compositions.

30 The compositions according to the present invention are preferably contacted to fabrics in a liquid form. Indeed, by "in a liquid form", it is meant herein the liquid compositions according to the present invention per se in neat or diluted form.

35 The compositions according to the present invention are typically used in diluted form in a laundry operation. By "in diluted form", it is meant herein that the compositions for the bleaching of fabrics according to the present

invention may be diluted by the user, preferably with water. Such dilution may occur for instance in hand laundry applications as well as by other means such as in a washing machine. Said compositions can be diluted up to 500 times, preferably from 5 to 200 times and more preferably from 10 to 5 80 times.

More specifically, the method of bleaching fabrics according to the present invention comprises the steps of first contacting said fabrics with a bleaching composition according to the present invention, in its diluted form, then 10 allowing said fabrics to remain in contact with said composition, for a period of time sufficient to bleach said fabrics, typically 1 to 60 minutes, preferably 5 to 30 minutes, then rinsing said fabrics with water. If said fabrics are to be washed, i.e., with a conventional composition comprising at least one surface active agent, said washing may be conducted together with the 15 bleaching of said fabrics by contacting said fabrics at the same time with a bleaching composition according to the present invention and said detergent composition, or said washing may be conducted before or after that said fabrics have been bleached. Accordingly, said method according to the present invention allows to bleach fabrics and optionally to wash fabrics with 20 a detergent composition comprising at least one surface active agent before the step of contacting said fabrics with said bleaching composition and/or in the step where said fabrics are contacted with said bleaching composition and/or after the step where said fabrics are contacted with the bleaching composition and before the rinsing step and/or after the rinsing step.

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In another embodiment of the present invention the method of bleaching fabrics comprises the step of contacting fabrics with a liquid bleaching composition according to the present invention, in its neat form, of allowing said fabrics to remain in contact with said bleaching composition for a period 30 of time sufficient to bleach said fabrics, typically 5 seconds to 30 minutes, preferably 1 minute to 10 minutes and then rinsing said fabrics with water. If said fabrics are to be washed, i.e., with a conventional composition comprising at least one surface active agent, said washing may be conducted before or after that said fabrics have been bleached. In the 35 embodiment of the present invention wherein the liquid bleaching composition of the present invention, is contacted to the fabrics in its neat form, it is preferred that the level of hypohalite bleach, is from 0.01% to 5%,

preferably from 0.1% to 3.5%, more preferably from 0.2% to 2% and most preferably from 0.2% to 1%. Advantageously, the present invention provides liquid hypohalite bleach-containing compositions that may be applied neat onto a fabric to bleach, despite a standing prejudice against using 5 hypochlorite-containing compositions neat on fabrics.

It is preferred to perform the bleaching methods herein before said fabrics are washed. Indeed, it has been observed that bleaching said fabrics with the compositions according to the present invention (diluted and/or neat 10 bleaching methods) prior to washing them with a detergent composition provides superior whiteness and stain removal with less energy and detergent than if said fabrics are washed first, then bleached.

Alternatively instead of following the neat bleaching method as described 15 herein above (pretreater application) by a rinsing step with water and/or a conventional washing step with a liquid or powder conventional detergent, the bleaching pre-treatment operation may also be followed by the diluted bleaching method as described herein before either in bucket (hand operation) or in a washing machine.

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Examples

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The invention is illustrated in the following non-limiting examples, in which all percentages are on a weight basis unless otherwise stated.

Composition (weight %)	I	II	III	IV
Sodium hypochlorite	3.5	3.5	3.5	5.0
Sodium hydroxide*	1.25	1.25	1.25	1.0
Sodium carbonate	3.0	3.0	3.0	1.2
Sodium silicate	0.5	0.5	0.5	0.5
Benzoic acid	0.5	-	1.0	0.5
Na C12-C14 E3S	7.0	7.0	7.0	7.0
Methoxy benzoate	0.5	1.0	-	0.5
Tinopal PLC®	0.01	0.01	0.01	0.01

Sodium tripolyphosphate (STPP)	0.1	0.1	0.1	-
Water and minors	up to 100%			

Composition (weight %)	V	VI	VII	VIII
Sodium hypochlorite	5.0	5.0	3.5	3.5
Sodium hydroxide*	1.0	1.0	1.25	1.25
Sodium carbonate	1.25	1.25	3.0	3.0
Sodium silicate	0.5	0.5	0.5	0.5
Benzoic acid	-	1.0	-	-
Na C12-C14 E3S	7.0	7.0	7.0	7.0
Methoxy benzoate	1.0	-	1.0	1.0
Tinopal PLC®	0.01	0.01	0.01	0.01
Phytic acid	-	-	-	1.0
Norasol 440N®	-	-	0.1	0.1
Sodium tripolyphosphate (STPP)	0.1	0.1	-	-
Water and minors	up to 100%			

Composition (weight %)	IX	X	XI	XII
Sodium hypochlorite	3.6	3.5	3.5	3.5
Sodium hydroxide*	1.25	1.25	1.25	1.25
Sodium carbonate	3.0	3.0	3.0	3.0
Sodium silicate	0.5	0.50	0.50	0.5
Benzoic acid	3.0	-	-	-
Na C12-C14 E3S	7.0	7.0	7.0	7.0
Sodium borate	-	-	3.0	3.0
Methoxy benzoate	-	1.0	1.0	1.0
Tinopal PLC®	-	-	-	0.01
Optiblanc BRB®	0.01	0.01	0.01	-
Sodium tripolyphosphate (STPP)	-	0.1	-	0.1
Water and minors	up to 100%			

Composition (weight %)	XIII	XIV	XV	XVI	XVII
Sodium hypochlorite	3.5	3.5	3.5	3.5	3.5
Sodium hydroxide*	1.25	1.25	1.25	1.25	1.25
Sodium carbonate	3.0	3.0	3.0	3.0	3.0
Sodium silicate	0.5	0.5	0.5	0.5	0.5
Sodium borate	-	-	-	-	-
Sodium tripolyphosphate (STPP)	0.1	0.1	0.1	0.1	0.1
Tinopal PLC®	0.01	0.01	0.01	-	-
Optiblanc BRB®	-	-	-	0.01	0.01
Phtalic acid	1.0	-	-	1.0	-
4-toluene sulfonic acid	0.5	1.0	--	-	1.0
2-nitrobenzoic acid	-	-	1.0	0.5	-
Water and minors	up to 100%				

Composition (weight %)	XVIII	XIX	XX	XXI
Sodium hypochlorite	3.5	3.5	3.5	3.5
Sodium hydroxide*	1.25	1.25	1.25	1.25
Sodium carbonate	3.0	3.0	3.0	3.0
Sodium silicate	0.5	0.5	0.5	0.5
Sodium borate	-	3.0	3.0	3.0
Sodium tripolyphosphate (STPP)	0.1	0.1	0.1	0.1
Tinopal PLC®	-	0.01	0.01	0.01
Optiblanc BRB®	0.01	-	-	-
Phtalic acid	-	1.0	-	-
4-toluene sulfonic acid	-	-	1.0	-
2-nitrobenzoic acid	1.0	1.0	-	1.0
water and minors	up to 100%			

* added NaOH

Tinopal PLC® is bis(sulfobenzofuranyl)biphenyl available from Ciba Geigy.

5 Optiblanc® is a stilbene derivative brightener available from 3 V Sigma.
 Na C12-C14 E3S is alkyl (ethoxy) 3 sulphate commercially available from Rhone Poulenc and Albright & Wilson.
 Benzoic acid is commercially available from Elf Atochem, Enichem, or Albright & Wilson.

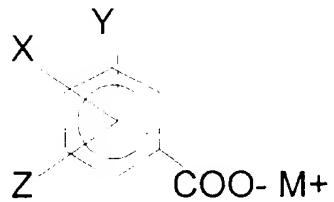
10 Methoxy benzoate is commercially available from Aldrich.
 Norasol 440N® is a polyacrylate polymer modified with phosphonic groups (MW 4000) from Norso Haas.

15 The compositions exemplified above exhibit effective whiteness performance when used to bleach fabrics both in neat or diluted conditions (e.g. at a dilution of 200 (typical dilution)) after 3 months of storage at room temperature (e.g. about 25°C) after their manufacturing.

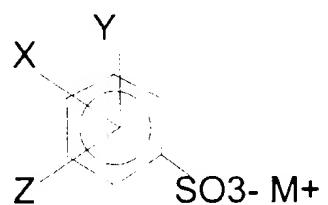
WHAT IS CLAIMED IS:

- 1- A liquid bleaching composition comprising:
 - a hypohalite bleach,
 - from 0.001% to 1% by weight of the total composition of a brightener
 - and a radical scavenger.
- 2- A composition according to claim 1 wherein said hypohalite bleach is an alkali metal sodium hypochlorite.
- 3- A composition according to any one of the preceding claims, wherein said hypohalite, based on active halide, is present in an amount of from 0.1% to 20% by weight, preferably from 0.25% to 8% by weight of the total liquid composition.
- 4- A composition according to any of the preceding claims wherein said brightener is a derivative of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanine, dibenzothiophene-5,5-dioxide, azole, 5- or 6-membered-ring heterocycle, naphthlimide, benzoxazole, benzofuran, benzimidazole or any mixture thereof, and more preferably is a derivative of stilbene.
- 5- A composition according to any one of the preceding claims, wherein the brightener or mixture thereof, is present in an amount of from 0.005% to 0.5% by weight, preferably from 0.005% to 0.3% by weight and more preferably from 0.008% to 0.1% by weight of the total liquid composition.
- 6- A composition according to any of the preceding claims wherein said radical scavenger is an aromatic radical scavenger or a mixture thereof, preferably a benzene derivative, naphthalene derivative, annulene derivative, cyclopentadiene derivative, cyclopropene derivative, aryl carboxylate, aryl sulfonate or a mixture thereof.
- 7- A composition according to any of the preceding claims wherein said radical scavenger has one of the following formulas:

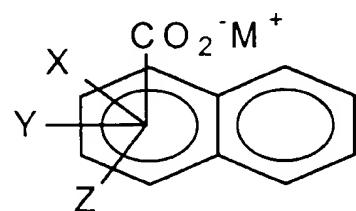
a)



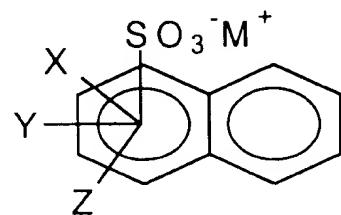
(b)



c)



d)



wherein each X, Y, and Z are -H, -COO-M⁺, -Cl, -Br, -SO₃-M⁺, -NO₂, -OCH₃, or a C₁ to C₁₀ primary and secondary alkyl groups and M is H or an alkali metal, or mixtures thereof, preferably said radical scavenger is phthalic acid; sulfophthalic acid; other mono-substituted phthalic acids; di-substituted benzoic acids; an alkyl-, chloro-, bromo-, sulfo-, nitro- or alkoxy- benzoic acid, i.e. where Y and Z are -H and X is a C₁ to C₁₀ primary and secondary alkyl groups, -Cl, -Br, -SO₃-H⁺, -NO₂, or -OCH₃ respectively or a substituted sulfonic acid, more preferably is benzoic acid, methoxy benzoic acid, 4-toluene sulfonic acid, 2 n-octyl benzoic acid, 3-nitro benzoic acid, 2 n-octyl sulfonic acid, anisic acid or mixtures thereof and most preferably is benzoic acid and/or methoxy benzoic acid and/or 3-nitro benzoic acid.

- 8- A composition according to any one of the preceding claims, wherein the radical scavenger or mixture thereof, is present in an amount of from 0.001% to 10% by weight, preferably from 0.01% to 8% by weight and more preferably from 0.1% to 6% by weight of the total liquid composition.
- 9- A composition according to any of the preceding claims, which further comprises a chelating agent of a mixture thereof up to a level of 10% by weight of the total composition, preferably from 0.01% to 5%, more preferably from 0.05% to 2%, and wherein said chelating agent preferably is a phosphonate chelating agent, phosphate chelating agent, polyfunctionally-substituted aromatic chelating agent, ethylenediamine N,N'- disuccinic acids, or a mixture thereof, and more preferably is sodium pyrophosphate, sodium tripolyphosphate, and/or phytic acid.
- 10- A composition according to any of the preceding claims which further comprises a pH buffering component typically in an amount of 0.5% to 9% by weight of the total composition, preferably from 0.5% to 5% by weight and more preferably from 0.6% to 3% by weight.

- 11- A composition according to claim 10, wherein said pH buffering component is selected from the group consisting of alkali metal salts of carbonates, polycarbonates, sesquicarbonates, silicates, polysilicates, boron salts, phosphates, stannates, alluminates, and mixtures thereof.
- 12- A composition according to any of the preceding claims, which further comprises a strong source of alkalinity.
- 13- A composition according to any of the preceding claims, which further comprises a polymer comprising monomeric units selected from the group consisting of unsaturated carboxylic acids, polycarboxylic acids, sulphonic acids, phosphonic acids, styrene sulphonic acid and mixtures thereof.
- 14- A composition according to any of the preceding claims, which further comprises an optional ingredient selected from the group consisting of bleach-stable surfactants, builders, thickening agents, pigments, dyes, solvents, perfumes, and mixtures thereof.
- 15- A method of bleaching fabrics which comprises the steps of:
 - contacting said fabrics with a liquid bleaching composition according to any of the preceding claims, in its diluted or neat form,
 - allowing said fabrics to remain in contact with said bleaching composition for a period of time sufficient to bleach said fabrics,
 - then rinsing said fabrics with water.
- 16- A method of bleaching fabrics according to claim 15 wherein the bleaching composition is diluted with water at a dilution level up to 500 times, preferably from 5 to 200 times and more preferably from 10 to 80 times.
- 17- A method according to any of the claims 15 or 16 wherein said fabrics are washed with a detergent composition comprising at least one

surface active agent before the step of contacting said fabrics with said bleaching composition and/or in the step where said fabrics are contacted with said bleaching composition in its diluted form and/or or after the step where said fabrics are contacted with the bleaching composition and before the rinsing step and/or after the rinsing step.

- 18- The use, in a liquid bleaching composition comprising a hypohalite bleach and a brightener, of a radical scavenger and/or a chelating agent, for effective whiteness performance upon ageing of the composition.
- 19- The use, in a liquid bleaching composition comprising a hypohalite bleach and a brightener, of a radical scavenger and/or a chelating agent, to improve the stability of said brightener in said composition.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/01345

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/395 C11D3/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 5 196 139 A (MOSCHNER KARL) 23 March 1993 see column 3, line 8 - line 26 see column 4, line 46 - line 48 see column 8, line 30 - line 41 see column 16, line 43 - column 17, line 45 --- EP 0 462 793 A (CLOROX CO) 27 December 1991 cited in the application see claims 12,13 see page 3, line 33 - line 35 see page 13, line 50 - page 14, line 13 --- -/--	1-5, 8, 13, 15, 18, 19
X		1-5, 10-14, 18, 19

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- V* document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- &* document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

26 October 1998

02/11/1998

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Authorized officer

Richards, M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/01345

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	US 3 666 680 A (BRIGGS BENJAMIN R) 30 May 1972 see column 2, line 29 - line 33 see column 7, line 44 - line 73 see column 5, line 63 - line 75 see column 6, line 67 - line 70 see column 7, line 36 - line 41 ---	1-8, 14, 18, 19
A	EP 0 156 438 A (PROCTER & GAMBLE) 2 October 1985 cited in the application see page 2, line 34 - page 3, line 25 ---	1-8, 14, 18, 19
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A	US 5 034 150 A (SMITH WILLIAM L) 23 July 1991 see column 4, line 58 - line 67 see column 6, line 64 - column 7, line 8 see column 5, line 61 - line 62 see column 7, line 32 - line 37 ---	1-3, 6-12, 14, 18, 19
A	EP 0 206 718 A (CLOROX CO) 30 December 1986 cited in the application see page 6, line 13 - line 16 see page 8, line 19 - line 27 see page 10, line 1 - line 6 see page 12, line 18 - line 19 ---	1-5, 10-13
A	US 4 900 468 A (MITCHELL JAMES D ET AL) 13 February 1990 see claims 1-11 -----	1, 4-11, 14

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Information on patent family members

International Application No

PCT/IB 98/01345

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 98/01345

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